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Calibration of potentiometric sensor arrays with a reduced number of standards

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ABSTRACT

In this paper a novel calibration procedure for the parameter determination of ion-selective electrodes used in an array is described. Commonly used procedures require a large number of standards to determine the parameters based on the Nicolsky–Eisenman model. The elaborated procedure reduces the number of standards to a minimum by using a standard containing a mixture of ions instead of a couple of pure standards. This paper presents a complete calibration procedure, which consists of designing the composition of the standards, parameter determination and verification of the calibration results. Comparison of the results obtained by the procedure presented with results obtained by the Two-Point Calibration and Separate Solution methods proves that the accuracies of both procedures are comparable. The outlined procedure can be applied in multicomponent analysers.

1. Introduction

Many factors influence the measured potential of an Ion-Selective Electrode (ISE). This results from the fact that electrode models [1–3] consist of a couple of parameters which have to be determined before measurements are taken by conducting a proper calibration procedure.

Electrodes have to be frequently calibrated, even before each assay, to obtain satisfactory accuracy [4]. In a case where the sensor array used consists of N ion-selective electrodes, the number of parameters which have to be determined grows N times in comparison with a single electrode. It is important to minimise the number of standard solutions to reduce the costs and time necessary to perform such operations.

The authors attempt to determine a calibration procedure that is more convenient to calibrate sensor arrays than those commonly used and recommended by IUPAC. There are procedures in the literature which are based on different optimisation methods, such as artificial neural networks [5], curve fitting [6] or Bayesian methods [7]. The procedure developed should minimise the number of standards needed to determine the calibration parameters of all ISEs in an array, even if the standards are carefully prepared mixtures of many substances.

In this paper, the procedure has been tested and the results are compared with the reference procedure.

2. Theory

There are many models describing the ISE phenomenon. Among them the oldest, and also most simple, is the Nernst equation [1] which describes a relationship between the electrode potential and the activity of the primary ion (ion of interest) in a case where the interfering ions have negligible impact.

The expanded version of the Nernst equation is the Nicolsky–Eisenman (N–E) equation. It takes into account the interfering ions as well. Even though it is not perfect and is criticised by some authors [2,8], it is most commonly applied and is recommended by IUPAC [9]. The term for the variant with the practical limit of detection has the following form [10,11]:

$$E_i = E^{\circ}{}_i + S_i \lg\left(a_i + \sum_{j \neq i} K_{ij} a_j^{z_i/z_j} + L_i\right) \tag{1}$$

where index i means the primary ion and j means the other ions present in the solution, E_i is the potential of the electrode selective to ion i, $E^{\circ}{}_i$ is the electrode standard potential, S_i is the electrode slope, K_{ij} is the potentiometric selectivity coefficient, a is the activity of the ion, z is the charge number of the ion and L_i is the practical limit of detection. The parameter L_i takes into consideration not only the electrode's limit of detection but also all other influences of interference ions not included in the term $\sum_{j \neq i} K_{ij} a_j^{z_i/z_j}$ for different reasons, such as not knowing the exact concentration values of ions in ionic strength/pH stabilisers or in contaminations.

It is obvious that if the number of model parameters decreases then the number of experiments needed to be performed to

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obtain their values also decreases. It is the reason why the authors have chosen the N–E model. They are convinced that this model is suitable to be applied in analysers as a compromise between complexity and accuracy.

Let us take into consideration an ISE array with N ISEs sensitive to different ions (more precisely: ISEs for which primary ions are different). If there is a need to determine all of the selectivity coefficients toward primary ions of the other ISEs then the number of all parameters N_P (E°_i, S_i, L_i and selectivity coefficients) needed to be determined for N electrodes is

$$N_P = N^2 + 2N \tag{2}$$

N potentials can be determined in each calibration standard. One measurement per parameter is necessary in the best case. The minimum number of calibration standards is equal to

$$\frac{N_P}{N} = \frac{N^2+2N}{N} = N+2 \tag{3}$$

To determine the parameters of electrodes according to IUPAC recommended procedures at least three standards are required to determination of E°_i, S_i, L_i [12], and at least two solutions for each K_{ij} [9] (separate solution method). The same solution with ion j for determination of K_{ij} can be used for the determination of E°_i, S_i of the ISE for which the given ion j is a primary ion. It means that the minimum number of standards is $3N$.

3. Area of application

The elaborated procedure allows one to not only determine the slope and standard potential of each ISE but also the practical limits of detection and selectivity coefficients. The practical limit of detection is important in measurements in which one expects low activities of ions in samples. Selectivity coefficients are important in samples with high activities of interfering ions. It means that the calibration procedure is tailored for application where the activities of ions vary in wide range. A reduction in the number of standards means that the calibration procedure can be usable in automated analysers with continuous measurements due to a lowering of costs and time for calibration. The procedure can be applied in medical analysers of urine samples, environmental measurements (rivers, lakes, wastewater), water monitoring in food industries or research on electrode arrays.

The purpose of the calibration procedure is to obtain the parameters which will be applied in measurements (as opposed to obtaining the best theoretical values). According to commonly used practice [13], the calibration should be performed in a way as far as possible similar to working conditions. Therefore, the measuring range and the span of activities in the standards should be similar, probes and standards should have similar background composition (*e.g.* from sample pretreatment), *etc.*

The calibration procedure developed is based on N–E model and can therefore be applied to ISEs for which the N–E model adequately describes their response.

4. Description of calibration procedure

The reduction in the number of standards is faced with an additional error, noted here as ΔpX_{Max}. The error has to be smaller than the acceptable uncertainty of activity measurements in a given application. Before starting the algorithm, the value of ΔpX_{Max} should be assumed.

The calibration procedure consists of several steps (Fig. 1). First, the values of parameters should be assumed (Step 1) according to the information obtained from ISE catalogue data, literature or prior experiments. It allows selecting activities in standard solutions (Steps 2 and 3). The next step (Step 4) is the experimental part in which the potentials of ISEs in standard solutions are determined and the values of the parameters are calculated. After that, it is necessary to check whether the requirements for standard solutions are fulfilled for determined values of ISE parameters (Steps 5–7). A detailed description of the procedure is provided below.

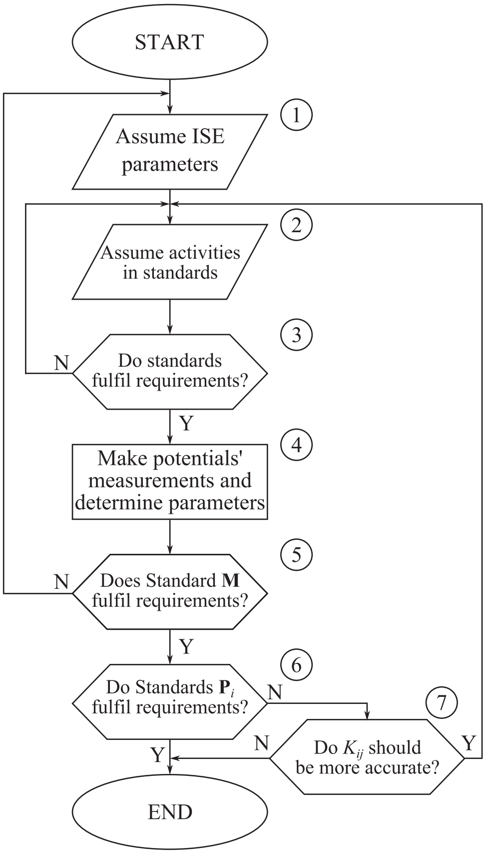

Fig. 1. Concept of calibration algorithm.

4.1. Required standard solutions

To determine all calibration parameters, the following standard solutions should be used:

- Standards $\mathbf{P}_i$—N pure solutions containing only ion i being the primary ion of the i-th electrode.
- Standard **M**—one mixture containing all compounds of interest.
- Standard **L**—one pure solvent (*e.g.* deionised water) used for the determination of the limits of detections.

This makes $N+2$ standards, and it is the minimum number of standards needed to determine all of the N–E parameters of N ISEs in an array. If any pretreatment procedures are applied to the samples before measurement, the same pretreatment should be applied to the standards—*e.g.* addition of ionic strength stabiliser.

4.2. Formulae of parameters

Formulae for the parameters' determination were derived from Eq. (1). In order for one to better imagine how the parameters are calculated, the calibration points are placed on

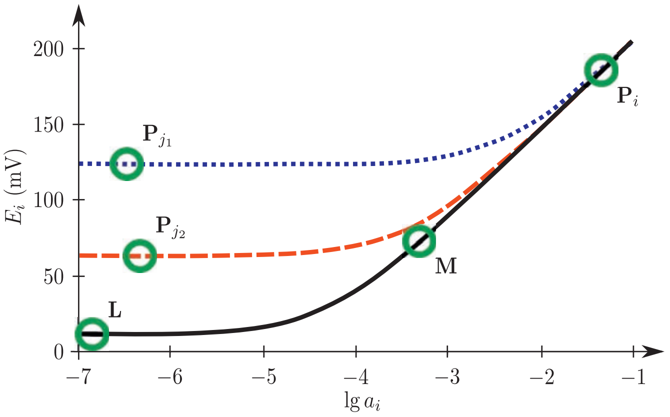

Fig. 2. Graphical interpretation of calibration procedure. Solid line represents the response of an ISE in a solution containing only primary ion i; dotted and dashed lines—in solutions containing constant activity of interfering ions j_1, j_2 and varying activity of the primary ion. Circles represent the calibration points described in the text.

an ISE characteristic in Fig. 2. Points $\mathbf{P}_i$ and **M** allow the determination of parameters $E^\circ{}_i$ and S_i. Potentials of the ISE selective to ion i in standards $\mathbf{P}_{j_1}$ and $\mathbf{P}_{j_2}$ are determined by activities of interfering ions j_1, j_2 and are used for the determination of the selectivity coefficients K_{ij_1}, K_{ij_2}, respectively. The value of L_i is estimated using the potential value of the ISE in Standard **L**.

Values of parameters are estimated from equations:

$$S_i = \frac{E_i(\mathbf{P}_i) - E_i(\mathbf{M})}{\lg a_i(\mathbf{P}_i) - \lg a_i(\mathbf{M})} \tag{4}$$

$$E^\circ{}_i = E_i(\mathbf{P}_i) - S_i \lg a_i(\mathbf{P}_i) \tag{5}$$

$$\lg K_{ij} = \frac{E_i(\mathbf{P}_j) - E^\circ{}_i}{\ln(10)\dfrac{RT}{z_i\mathrm{F}}} - \lg\left[a_j(\mathbf{P}_j)\right]^{z_i/z_j} \tag{6}$$

$$L_i = \frac{E_i(\mathbf{L}) - E^\circ{}_i}{S_i} \tag{7}$$

where $E_i(\mathbf{P}_i)$, $E_i(\mathbf{M})$, $E_i(\mathbf{P}_j)$, $E_i(\mathbf{L})$ are potentials of the i-th electrode in standards $\mathbf{P}_i$, **M**, $\mathbf{P}_j$ and **L**, respectively; $a_i(\mathbf{M})$, $a_i(\mathbf{P}_i)$, $a_j(\mathbf{P}_j)$ are activities of ion i in the **M**, $\mathbf{P}_i$ standards and activity of ion j in the $\mathbf{P}_j$ standard, respectively.

4.3. *Requirements for calibration solutions*

Standard **M** is used to determine the slopes S_i using Eq. (4) and the standard potentials $E^\circ{}_i$ using Eq. (5). It is important to compose the mixture of ions in such a way that the potential of each ISE selective to ion i is determined by the activity of the primary ion i, and not by the interfering ions or its limit of detection L_i. The theoretical value of error of potential caused by interfering ions and the limit of detection can be estimated from N–E Eq. (1). In order to do that, Eq. (1) can be transformed into

$$E_i = E^\circ{}_i + S_i \lg\left[a_i(\mathbf{M}) + \phi_i\right] \tag{8}$$

where ϕ_i is the sum of interferences

$$\phi_i = \sum_{j \neq i} K_{ij} a_j(\mathbf{M})^{z_i/z_j} + L_i \tag{9}$$

Therefore the value of the error is

$$\Delta E_i = S_i[\lg(a_i(\mathbf{M}) + \phi_i) - \lg a_i(\mathbf{M})] = S_i \lg\left(\frac{a_i(\mathbf{M}) + \phi_i}{a_i(\mathbf{M})}\right) \tag{10}$$

ΔE_i is the systematic error which can be eliminated.

If the maximum value of the systematic error, expressed in logarithm scale of activity, is assumed to be ΔpX_{Max} then the lowest required activity $a_i(\mathbf{M}_{\mathrm{Req}})$ of the primary ion i in Standard **M** could be calculated as

$$a_i(\mathbf{M}_{\mathrm{Req}}) = \frac{\phi_i}{10^{\Delta pX_{\mathrm{Max}}} - 1} \tag{11}$$

and the activity of ion i in Standard **M** should fulfil the following condition:

$$a_i(\mathbf{M}) > a_i(\mathbf{M}_{\mathrm{Req}}) \tag{12}$$

E.g., if $\Delta pX_{\mathrm{Max}} = 0.1$ and for ISE selective to ion i is $\phi_i = 10^{-5}$ then activity $a_i(\mathbf{M})$ should be greater than 3.9×10^{-5}.

Eq. (12) should be fulfilled during the preparation of Standard **M** (Step 3) and during the verification of the calibration results (Step 5). Such calculations have to be performed for each ion i in Standard **M**.

If it is impossible to satisfy Eq. (12) then Standard **M** has to be replaced by two or more standards for which requirement (12) is fulfilled.

Standard $\mathbf{P}_i$ is used for the determination of $E^\circ{}_i$, S_i and K_{ji}. To estimate values of $E^\circ{}_i$ and S_i as correctly as possible, activities of ions in Standards $\mathbf{P}_i$ should be as high as possible and about 100 times greater than the activity of ion i in Standard **M**, to reduce the influence of potential measurement accuracy [3].

The same standards are also used to estimate selectivity coefficients. Ion i is the primary ion for the i-th ISE, and simultaneously the interfering ion for other ISEs. In order to properly estimate the selectivity coefficient K_{ji}, the activity of ion i should determine the potential of the j-th ISE in Standard $\mathbf{P}_i$. This leads to a formula similar to (12) for Standard **M**. The systematic error caused by interferences is

$$\Delta E_{ji} = \ln(10)\frac{RT}{z_j\mathrm{F}}\left[\lg\left(K_{ji}a_i(\mathbf{P}_i)^{z_j/z_i} + \psi_{ji}\right) - \lg\left(K_{ji}a_i(\mathbf{P}_i)^{z_j/z_i}\right)\right] \tag{13}$$

where sum of interferences ψ_{ji} is defined as

$$\psi_{ji} = a_j(\mathbf{P}_i) + \sum_{k \neq i,j} K_{jk} a_k(\mathbf{P}_i)^{z_j/z_k} + L_j \tag{14}$$

and $a_j(\mathbf{P}_i)$, $a_k(\mathbf{P}_i)$ are the activities of ions in Standard $\mathbf{P}_i$ which can come out of the contamination of the standard. Even the purest of standards have contamination (trace elemental impurities) which limit the determination range of the K_{ji} values [14].

The requirement for activity $a_i(\mathbf{P}_{i,\mathrm{Req}})$ in Standard $\mathbf{P}_i$ can be derived from (10) in the same way as Eq. (12) is derived from (10)

$$a_i(\mathbf{P}_{i,\mathrm{Req}}) = \left(\frac{\psi_{ji}}{K_{ji}(10^{\Delta pX_{\mathrm{Max}}} - 1)}\right)^{z_i/z_j} \tag{15}$$

and

$$a_i(\mathbf{P}_i) > a_i(\mathbf{P}_{i,\mathrm{Req}}) \tag{16}$$

The requirement has to be fulfilled when the composition of Standard $\mathbf{P}_i$ is set (Step 3), and it is verified during validation of the calibration results (Step 6).

It may occur that for the maximal allowable activity a_i, the logarithm of selectivity coefficient cannot be determined with the assumed maximum systematic error ΔpX_{Max} (Step 7). Even if in the pure solution $\mathbf{P}_i$ used for the determination of K_{ji} the activity of ion i does not determine the potential of ISE selective to ion j, the influence of ion i on the potential of the electrode can be omitted in measurements. Determination of the value of the selectivity coefficient in such a case can be regarded as checking whether the selectivity coefficient is small enough and its correct value is not necessary during measurements.

Standard **L** is used for the determination of the values of practical limits of detection L_i of all electrodes under given conditions. It is a solvent with no ions added, unless in the case of pretreatment. Unfortunately, the potentials of the electrodes in Standard **L** can be unstable. The conductance of solution is very low and electromagnetic interferences can generate additional voltages. Even low contamination from the atmosphere (*e.g.* CO_2), membranes or apparatus can dramatically change the activities of ions in a very dissolved solution. For this reason, the determined value of L_i is instead informational, but is very important to estimate the measuring range.

4.4. Data analysis after measurements

At Step 4, the measurements of the ISE potentials in standards **M**, $\mathbf{P}_i$, **L** are conducted and the parameters' values from Eqs. (4)–(7) are determined. After that, tests should be performed to validate the values of the parameters. If requirements (12) and (16) are fulfilled, it can be assumed that the calibration procedure was performed correctly.

If formula (12) is not fulfilled for ion i (Step 5) then all parameters of ISE for which it is the primary ion are determined with insufficient accuracy. In such a case Standard **M** should be changed.

If formula (16) is not fulfilled for ion i for ISE selective to ion j (Step 6), then the selectivity coefficient K_{ji} is so small that it is impossible to determine the value of $\lg K_{ji}$ with the assumed maximum error ΔpX_{Max}. If it is necessary to determine the value with better accuracy (Step 7), then the activity of ion i in Standard $\mathbf{P}_i$ should be increased as greatly as possible.

5. Experimental

5.1. Reagents

Analytically pure salts of NaCl, KCl and LiCl, obtained from POCH, Gliwice, Poland, have been used to prepare all concentration standards. The ionophores: potassium ionophore I, sodium ionophore III (ETH 2120), lithium ionophore VIII, lipophilic salt: potassium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (KTFPB), plasticizers: bis(2-ethylhexyl)adipate (DOA), bis(1-butylpentyl)adipate (BBPA) and poly(vinyl chloride) (PVC, high molecular weight) were Selectophore reagents obtained from Fluka AG, Buchs, Switzerland and used as membrane components. Deionised water (0.1 $\mu S\ cm^{-1}$) and Pyrex class A glassware was used for the preparation of all solutions.

5.2. Membrane preparation and sensor construction

Membranes were prepared with the application of the method described in the Selectophore catalogue [15]. The composition of K^+-selective membrane is 2% (w/w) of potassium ionophore I, 1.2% (w/w) of KTFPB, 64% (w/w) of DOA and 32.8% (w/w) of PVC. The composition of the Na^+-selective membrane was after [16] and that of Li^+-selective membrane was after [17].

The Na^+, K^+ and Li^+ membranes were mounted onto a Philips type IS-561 electrode body (Gläsblaserei Möller, Zurich, Switzerland) and filled with 0.01 mol L^{-1} solution of NaCl, KCl and LiCl, respectively. The three electrodes, together with the RL100 double junction reference electrode (Hydromet, Gliwice, Poland), comprised the electrode array. The K^+ electrode was one year old and used under various conditions.

5.3. Instrumentation and software

All measurements have been performed using a multichannel ion-meter described elsewhere [18,19], with 0.5 mV expanded uncertainty in a ±1000 mV measuring range during potential measurements under a controlled temperature of $(25 \pm 1)\ ^\circ C$. Short-term precision (repeatability) of measurements expressed as a standard deviation is less than 0.01 mV.

Activity of Na^+, K^+ and Li^+ ions in standards had been determined with the use of a Pitzer model [20] using PHREEQC software [21]. The liquid junction potential has been estimated with the application of the Henderson equation [22,23].

Estimation of the parameter values has been performed using MS Excel 2003.

5.4. Measurement sequence

The standards of activities have been made according to Table 1. Standards $\mathbf{P}_{Na}$, $\mathbf{P}_{K}$, $\mathbf{P}_{Li}$, **M**, **L** are used in the elaborated procedure. Standards $\mathbf{P}_{Na}$, $\mathbf{P}_{K}$, $\mathbf{P}_{Li}$, $\mathbf{R}_{Na}$, $\mathbf{R}_{K}$, $\mathbf{R}_{Li}$, **L** are used in the reference procedure.

Five series of calibration procedures have been performed. Each series consists of potentials' measurements of the electrode array immersed in standards in the following order: **L**, $\mathbf{R}_{Na}$, $\mathbf{P}_{Na}$, **L**, $\mathbf{R}_{K}$, $\mathbf{P}_{K}$, **L**, $\mathbf{R}_{Li}$, $\mathbf{P}_{Li}$, **M**. The electrode array has been immersed in each standard for 3.5 min. The mean of the voltages recorded during the final 30 s has been assumed as the electrode potential.

5.5. Elaborated procedure

According to the algorithm, the ion activities in standards have been selected as a first step. Next, the requirements for ions activities in standards **M** and $\mathbf{P}_i$ have been verified. The results of the verification have been gathered in Tables 2 and 3. At this stage one can say that all standards are correctly composed.

Using the data obtained from the potentials' measurements, slopes S_i using Eq. (4) and the standard potentials $E^\circ{}_i$ using Eq. (5) have been calculated. The selectivity coefficients K_{ji} and limits of detection L_i have been determined using Eqs. (6) and (7), respectively.

Table 1
Composition of standards used in the experiments $\left(c^0 = 1\ \text{mol L}^{-1}\right)$. Contamination of salts used for standard preparation are taken into account.

Standard	$-\lg \frac{c_{Na}}{c^0}$	$-\lg \frac{c_K}{c^0}$	$-\lg \frac{c_{Li}}{c^0}$	$-\lg a_{Na}$	$-\lg a_K$	$-\lg a_{Li}$
$\mathbf{P}_{Na}$	1.00	4.29	6.00	1.10	4.41	6.10
$\mathbf{P}_{K}$	4.42	1.00	6.00	4.52	1.11	6.10
$\mathbf{P}_{Li}$	4.06	4.06	1.01	4.16	4.17	1.11
M	3.00	4.51	3.53	3.02	4.51	3.55
$\mathbf{R}_{Na}$	3.00	6.29	8.00	3.01	6.31	8.01
$\mathbf{R}_{K}$	6.42	3.00	8.00	6.43	3.01	8.01
$\mathbf{R}_{Li}$	6.06	6.06	3.01	6.08	6.08	3.02
L	Deionised water			Deionised water		

Table 2
Preliminary comparison of the assumed ion activities $a_i(\mathbf{M})$ in Standard **M** with activities $a_i(\mathbf{M}_{\text{Req}})$ according to Eq. (12). ISE parameters are obtained from manufacturers' data, $\Delta pX_{\text{Max}} = 0.1$. Step 3 of the algorithm.

Ion i	$\lg a_i(\mathbf{M})$	$\lg a_i(\mathbf{M}_{\text{Req}})$	Test
Na^+	−3.02	−3.95	Pass
K^+	−4.31	−4.55	Pass
Li^+	−3.55	−4.27	Pass

Table 3
Preliminary comparison of the assumed ion activities $a_i(\mathbf{P}_i)$ in Standards $\mathbf{P}_i$ with activities $a_i(\mathbf{P}_{i,\text{Req}})$ according to Eq. (16). ISE parameters are obtained from manufacturers' data, $\Delta pX_{\text{Max}} = 0.1$. Step 3 of the algorithm.

$\mathbf{P}_i$	lg $a_i(\mathbf{P}_i)$	$K_{j,i}$	lg $a_i(\mathbf{P}_{i,\text{Req}})$	Test
$\mathbf{P}_{\text{Na}}$	−1.10	$K_{\text{K,Na}}$	−1.29	Pass
		$K_{\text{Li,Na}}$	−1.97	Pass
$\mathbf{P}_{\text{K}}$	−1.11	$K_{\text{Na,K}}$	−2.31	Pass
		$K_{\text{Li,K}}$	−2.07	Pass
$\mathbf{P}_{\text{Li}}$	−1.11	$K_{\text{Na,Li}}$	−2.31	Pass
		$K_{\text{K,Li}}$	−1.17	Pass

5.6. *Reference procedure*

Two-Point Calibration has been applied to determine the parameters S_i, $E^\circ{}_i$. These values have been calculated using

$$S_i = \frac{E_i(\mathbf{R}_i) - E_i(\mathbf{P}_i)}{\lg a_i(\mathbf{R}_i) - \lg a_i(\mathbf{P}_i)} \tag{17}$$

$$E^\circ{}_i = E_i(\mathbf{P}_i) - S_i \lg a_i(\mathbf{P}_i) \tag{18}$$

Selectivity coefficients K_{ij} have been determined using

$$\lg K_{ij} = \frac{E_i(\mathbf{P}_j) - E_i(\mathbf{P}_i)}{\ln(10)\dfrac{RT}{z_i\mathrm{F}}} + \left(1 - \frac{z_i}{z_j}\right) \lg a_i(\mathbf{P}_i) \tag{19}$$

Limits of detections L_i have been determined using

$$L_i = \frac{E_i(\mathbf{L}) - E^\circ{}_i}{S_i} \tag{20}$$

6. Results and discussion

Experiments of the comparison between the elaborated calibration procedure with the reference procedure have been performed for three ISEs selective to Na^+, K^+ and Li^+ ions. The K^+-selective electrode has been intentionally chosen as old to illustrate the algorithm working in a case where the actual parameters of the electrode differ from catalogue data.

Two-Point Calibration has been used as the reference procedure because it is the most frequently applied in practice [3]. The selectivity coefficients are calculated according to Separate Solution Method ($a_A = a_B$) [9]. In fact, the concentrations, not the activities, were equal to each other, but it causes an error in the estimation of K_{ij} below 1%. Accuracy of K_{ij} determination is often worse. IUPAC recommends a graphical intersection method of determination of the limit of detection [12]. The authors have chosen a computational method using a modified N–E equation (1) corresponding to IUPAC method.

When comparing both methods, one can say that the reference procedure requires $2N+1$ pure solutions in order for all parameters to be determined. In the elaborated procedure, $N+2$ standard solutions are required. This results from replacing N reference standards $\mathbf{R}_i$ with one mixed standard $\mathbf{M}$.

The results of the experiments are gathered in Table 4. According to Steps 5 and 6 of the algorithm, the ion activities in Standards $\mathbf{M}$ and $\mathbf{P}_i$ are verified with respect to the value of error ΔpX_{Max}, which is less than 0.1. The results are gathered in Tables 5 and 6. One can conclude that all standards are correctly prepared; except for standards $\mathbf{P}_{\text{Na}}$ and $\mathbf{P}_{\text{Li}}$ where the activities of ions of Na^+ and Li^+, respectively, are too low to properly estimate the values of $K_{\text{K,Na}}$ and $K_{\text{K,Li}}$. According to Step 7 of the algorithm, activities in standards $\mathbf{P}_{\text{Na}}$ and $\mathbf{P}_{\text{Li}}$ should be modified to determine the selectivity coefficients $K_{\text{K,Na}}$, $K_{\text{K,Li}}$ with the assumed accuracy.

Table 4
Comparison of parameters' values obtained by the elaborated procedure (Elab. proc.) and by the reference procedure (Ref. proc.). The values are the means from five calibration experiments. (Elab. − Ref.)—differences between the mean values. (SD Elab.) and (SD Ref.)—standard deviations of parameters' values using elaborated and reference procedures, respectively.

ISE	Parameter	Elab. proc.	Ref. proc.	Elab.− Ref.	SD Elab.	SD Ref.
Na	$E^\circ{}_{\text{Na}}$ (mV)	282.4	283.2	−0.9	0.6	0.7
	S_{Na} (mV)	55.9	56.7	−0.8	0.3	0.5
	lg L_{Na}	−5.46	−5.40	−0.06	0.15	0.15
	lg $K_{\text{Na,K}}$	−1.75	−1.82	−0.07	0.01	0.01
	lg $K_{\text{Na,Li}}$	−0.84	−0.90	−0.06	0.02	0.01
K	$E^\circ{}_{\text{K}}$ (mV)	256.2	255.8	0.4	0.3	0.3
	S_{K} (mV)	49.1	48.8	0.4	0.1	0.3
	lg L_{K}	−7.09	−7.13	0.05	0.30	0.32
	lg $K_{\text{K,Na}}$	−3.06	−3.24	0.18	0.02	0.01
	lg $K_{\text{K,Li}}$	−3.18	−3.36	0.18	0.16	0.16
Li	$E^\circ{}_{\text{Li}}$ (mV)	298.0	299.0	−1.0	2.4	2.1
	S_{Li} (mV)	61.1	62.0	−0.9	0.1	0.2
	lg L_{Li}	−5.48	−5.42	−0.06	0.35	0.36
	lg $K_{\text{Li,Na}}$	−2.28	−2.24	−0.04	0.01	0.01
	lg $K_{\text{Li,K}}$	−3.36	−3.33	−0.03	0.03	0.03

Table 5
Final comparison of ion activities $a_i(\mathbf{M})$ in Standard $\mathbf{M}$ with activities $a_i(\mathbf{M}_{\text{Req}})$ according to Eq. (12). ISE parameters are calculated using the elaborated procedure, $\Delta pX_{\text{Max}} = 0.1$. Step 5 of the algorithm.

Ion i	lg $a_i(\mathbf{M})$	lg $a_i(\mathbf{M}_{\text{Req}})$	Test
Na^+	−3.02	−3.75	Pass
K^+	−4.31	−5.37	Pass
Li^+	−3.55	−4.49	Pass

Table 6
Final comparison of ion activities $a_i(\mathbf{P}_i)$ in Standards $\mathbf{P}_i$ with activities $a_i(\mathbf{P}_{i,\text{Req}})$ according to Eq. (16). ISE parameters are calculated using the elaborated procedure, $\Delta pX_{\text{Max}} = 0.1$. Step 6 of the algorithm.

$\mathbf{P}_i$	lg $a_i(\mathbf{P}_i)$	$K_{j,i}$	lg $a_i(\mathbf{P}_{i,\text{Req}})$	Test
$\mathbf{P}_{\text{Na}}$	−1.10	$K_{\text{K,Na}}$	−0.76	Fail
		$K_{\text{Li,Na}}$	−2.52	Pass
$\mathbf{P}_{\text{K}}$	−1.11	$K_{\text{Na,K}}$	−2.13	Pass
		$K_{\text{Li,K}}$	−1.42	Pass
$\mathbf{P}_{\text{Li}}$	−1.11	$K_{\text{Na,Li}}$	−2.71	Pass
		$K_{\text{K,Li}}$	−0.40	Fail

A comparison between the parameters obtained with the application of the elaborated and reference procedures (Table 4) are as follows: Parameters $E^\circ{}_i$ and S_i for all of the electrodes are determined within the difference of 1 mV. A standard deviation of $E^\circ{}_i$ calculated for a lithium electrode is the worst and about 10 times worse than for a potassium electrode. The probable cause is a drift of electrode potential noted during the measurements (data not included in the paper). The differences in practical limits of detections determination are at the level of 0.1 in log scale. The standard deviations of the parameter are greater. It means that the difference between means is not statistically significant. Differences between selectivity coefficients for the sodium and lithium electrodes are below 0.1 in log scale. Differences for potassium electrode are much worse. This is caused by the fact that the sensitivity of the electrode is significantly lower than the Nernstian value, and results from using electrode characterized by parameters departing from those assumed. The great number of steps in the elaborated procedure might seem to be a disadvantage. However, in other calibration procedures it is also necessary to carefully consider the selection of calibration standards and analyse the results after measurements. In practice, during calibrations performed repetitively under similar conditions, only Step 4 is executed and the values of the parameters are compared with previously obtained values.

7. Conclusions

The above results prove that the elaborated calibration procedure can replace commonly applied parameters' determination procedures when simultaneously using many different ion-selective electrodes. The procedure can be applied in automatic multi-component analysers because the reduction in the number of standard solutions reduces the calibration time and the storage requirements of standards.

The parameters' errors obtained by the elaborated procedure are comparable with the errors obtained using Two-Point Calibration and Separate Solution Method, despite the reduction of the calibration points.

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